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A series of surface-active, functionalized anilines were polymerized at fluid interfaces. By carefully maintaining isobaric conditions, kinetic and derived thermodynamic activation parameters were determined. The substitution position of the alkyl moiety on the aniline ring and the applied surface pressure was found to strongly influence the kinetics. Further analysis allowed a two rate constant model to be developed. The experiments were also extended to the polymerization of thin films at a planar liquid/liquid interface.		14. SUBJECT TERMS
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Kenneth J. Wynne, Scientific Officer

REVISED FINAL REPORT

**CHEMICAL REACTIVITY AS A FUNCTION OF MOLECULAR DISTANCE AND
ORIENTATION: A FUNDAMENTAL STUDY OF OXIDATIVE COUPLING
POLYMERIZATION**

by

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January 9, 1997

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Objective, Results, and Conclusions

Investigation of the effect of various environmental parameters on reactivity of 2-alkyl anilines was proposed. The proposed approach was to confine the reaction to fluid surfaces and investigate the kinetics with a Langmuir trough.

We have synthesized and examined the surface pressure vs. mean molecular isotherms of three alkyl substituted anilines, *ortho*-,*meta*- and *para*-pentadecylaniline, on aqueous subphases using LB techniques to study their surface orientation and packing behavior. All 3 isomers were found to be amphiphilic, with increasingly good surface packing as the substitution neared *para*. The surface properties (steep pressure increase and compact surface area) indicated the *para* compound formed condensed monolayer films with little orientational rearranging below the collapse pressure, in strong contrast to the *ortho* compound. At the onset of the π -area isotherm, it is believed that the hydrophilic amine group of the amphiphile is submersed in the aqueous phase with the first few methylene units on the alkyl chain in *gauche* conformations as it tries to escape the aqueous subphase. As the surface pressure is increased, the aniline's orientation at the interface is slowly changed, as characterized by the large compressibility, and the amine and alkyl groups are pushed up and away from the aqueous subphase.

Subsequently, we examined oxidative coupling polymerization in two-dimensions, also using Langmuir Blodgett techniques. The polymerizations were systematically studied by varying the Temperature, applied surface pressure, and subphase oxidant ($(NH_4)_2S_2O_8$) and acid (H_2SO_4). The reaction was monitored by measuring the change in mean molecular area and the average barrier speed (the rate of barrier displacement needed to maintain isobaric conditions) with time. The monotonic decrease in area during polymerization is due to the replacement of van der Waals radii by covalent bonds between monomer molecules and changes in their conformation. Both the *meta* and *ortho* compounds polymerized, however no polymer was obtained from the third isomer. Overall, it was shown that the method also yields, fast, reproducible results, and requires only sub-milligram quantities of material.

The polymerization kinetics results were subsequently analyzed by three different techniques: A) a single rate constant technique for monolayer polymerization, first developed by Gee and Rideal, which is an average of all the rate constants in the polymerization, B) a two rate constant method developed by our group and Prof. H. Reiss of UCLA, which takes into account that there is a initial step (two monomers coupling to form dimer) and a subsequent "propagation" step (monomer coupling with oligomer or polymer), C) a third kinetic equation proposed by Wei et al., which also tries to account for the autoacceleration behavior of the polymerization by expressing the rate in terms of two rate constants.

The activation energy was calculated from the Arrhenius law, and compared for the different isomers at various pressures. It was found that there was a marked increase in the polymerization rate of *ortho*-pentadecylaniline as the surface pressure increased (in fact, no reaction is measured without applied surface pressure). The activation area of *ortho*-pentadecylaniline was calculated using method A from the slope of the $\ln k$ vs. applied surface pressure plot. The values of ΔA^* of the 2 isomers were also compared, indicating that the activated complex is not only bimolecular but that ions of the same sign approach during it's formation. An interesting feature of the polymerizable isomers was that they lead to an identical product.

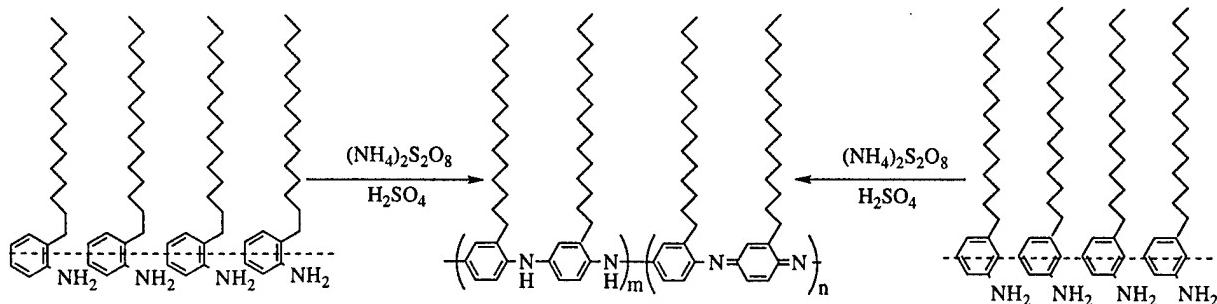


Figure 1. Monolayers of *ortho* and *meta* alkyl aniline monomers have different chemical reactivity, but lead to the same polymer.

The proposed mechanism of *ortho*-alkylaniline polymerization suggested that polymer growth is intermediate between classical step growth and chain growth mechanisms. Both *ortho*- and *meta*-showed an induction period during polymerization. Early on in our studies it was believed that this effect could be explained in terms of differences between the oxidation potentials of the monomer and oligomers; the monomer has a higher oxidation potential. Once oligomers form in the monolayer, they oxidize faster than monomer and the reaction rate accelerates. Subsequently, high molecular polymer was detected early on in the reaction suggesting a chain growth mechanism. This is in contradiction with forming low molecular oligomers in the early stages of the reaction that will accelerate polymer formation. Our data suggest that the polymer itself is involved in the process.

We subsequently demonstrated the feasibility of studying the same reactions at a planar liquid/liquid interface. This should allow for systematic characterizations of such polymerizations to be initially performed on idealized planar monolayers and subsequently applied to curved micellar surfaces.

Three other amphiphilic monomers, *ortho* and *meta* (1-octadecynyl)aniline and 17-(2-aminophenyl)heptadecanoic acid (Monomers 4-6 below), have been synthesized, characterized, spread to form stable monolayers at the aqueous-air interface, and polymerized under oxidative conditions. These were all polymerized as well.

The conclusions resulting from the work are:

- The Langmuir Blodgett technique may be used as an effective means of quantitatively studying polymerization kinetics under a vast range of parameter space.
- The polymerizations investigated at aqueous/air interfaces could be extended to liquid/liquid interfaces.
- New insight into the polymerization mechanism was revealed.
- A series of new monomers functionalized to have the potential for broader practical applications was synthesized.

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Publications:

1. H. Zhou, R. Stern, C. Batich, R. S. Duran, "The Polymerization of a Functionalized Aniline Monolayer", *Makromol. Chem., Rapid Commun.*, **11**, 409 (1990).
2. H. Zhou, R. Stern, C. Batich, R. S. Duran, "The Polymerization of Pentadecylaniline by Langmuir-Blodgett Techniques", *Polymer Preprints*, **31**(2), 560 (1990).
3. R. R. Bodalia, R. S. Duran, "The Effect of the Alkyl Side Chain Length on Stability and Polymerization of 2-Alkylanilines Using the Langmuir-Blodgett Technique", *Polymer Preprints*, **32**(1), 248 (1991).
4. H. C. Zhou, R. S. Duran, "The Effect of Surface Pressure on the Langmuir-Blodgett Polymerization of 2-Pentadecyl Aniline", *Polymer Preprints*, **32**(1), 202 (1991).
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6. H. Zhou and R. S. Duran, "Real Time Investigations of the Polymerization of 2-Pentadecyl Aniline on the L-B Trough", *Thin Solid Films*, **210/211**, 356 (1992).
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8. R. C. Advincula, R. S. Duran, J. LeMoigne and A. Hilberer, "Substituted Polyacetylenes at the Air-Water Interface", *Polymer Preprints*, **33**(2), 272 (1992).

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11. J. Adams, W. Rettig and R. S. Duran, "Langmuir Films of Liquid Crystalline Materials: The Influence of Molecular Architecture on Morphology and Properties", *J. Phys. Chem.*, **97**, 2021 (1993).
12. W. M. Sigmund and R. S. Duran, "Chemical Polymerization of 2-Pentadecylaniline Confined to a Planar Liquid/Liquid Interface", *Macromolecules*, **26**, 2616 (1993).
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16. R. S. Duran, W. Sigmund, T. Bailey and M. Hara, "Langmuir Blodgett and STM Investigation of Conducting Polymer Thin Films", *Polymer Preprints*, **35**(1), 219 (1994).
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18. P. Quint, T. Bailey, W. Sigmund, M. Hara, W. Knoll, H. Sasabe and R. S. Duran, "LB-Deposited, Side-Chain Substituted Polyaniline, Polypyrrole and the Corresponding Monomers, Studied by STM", *Polymer Preprints*, **35**(1), 281 (1994).
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22. T. K. Servay, A. Simmons, D. Tindall, T. Herod and R. S. Duran, "Langmuir-Blodgett Films of Copolypyrrroles", *Polymer Preprints*, **36**(1), 582 (1995).
23. T. Herod and R. Duran, "Polymerization and Phase Behavior of Poly(2-pentadecylaniline) and Liquid Crystal Mixtures at the Air-Water Interface", *Polymer Preprints*, Am. Chem. Soc., Div. Polym. Chem., **36**(1), 576 (1995).
24. L. J. Kloepfner, C. K. Nguyen, and R. S. Duran, "Alkyl Side Chain Positional Effect on the Polymerization of Alkyylaniline by Langmuir-Blodgett Techniques", *Polymer Preprints*, Am. Chem. Soc., Div. Polym. Chem., **36**(1), 580 (1995).
25. M. J. Roberts, W. W. Shen, T. J. Servay, R. C. Advincula, R. Awartani, M. A., Meador and R. S. Duran, "Langmuir and Langmuir-Blodgett-Kuhn Films of Mesogen Substituted Acetylene Monomers", submitted to *Thin Solid Films*.
26. W. M. Sigmund, C. Marestin, S. Keil, H. Zhou, M. Z. Elsabee, J. Ruhe, G. Wegner and R. S. Duran, "Chemical Polymerization and Langmuir-Blodgett Techniques - 2", submitted to *Macromolecules*.
27. T. Herod and R. Duran, "Phase and Domain Behavior of Conducting Polymer and Liquid Crystal Mixtures at the Air/Water Interface", submitted to *Langmuir*.

Presentations:

1. ACS National Meeting, Atlanta, GA, April 1991, "The Effect of the Alkyl Side Chain Length on Stability and Polymerization of 2-Alkylanilines Using the Langmuir-Blodgett Technique"
2. ACS National Meeting, Atlanta, GA, April 1991, "The Effect of Surface Pressure on the Langmuir-Blodgett Polymerization of 2-Pentadecyl Aniline"
3. ACS National Meeting, Atlanta, GA, April 1991, "Density Measurements on Poly(styrenes) of Different Tacticities"
4. ACS National Meeting, Atlanta, GA, April 1991, "Blends of Side Chain Liquid Crystalline Polymers at the Air-Water Interface"
5. ACS National Meeting, Atlanta, GA, April 1991, "Behavior of Liquid Crystalline Acetylenic Compounds at the Air-Water Interface"
6. 5th International Conference on Langmuir-Blodgett Films, Paris, France, August 26, 1991, "Ferroelectric Liquid Crystals at the Air/Water Interface"
7. 5th International Conference on Langmuir-Blodgett Films, Paris, France, August 26, 1991, "Real Time Investigations of the LB Polymerization of 2-Pentadecyl Aniline"
8. International Conference on Speciality Polymers 1991, Mainz, Germany, September 30, 1991, "Characterization of Monolayers on Free Surfaces: LB Investigations of Conducting and Liquid Crystalline Polymers"
9. Gordon Conference Polymers/West, January 1992, "Polymerization Reactions Restricted to Free Surfaces"
10. Florida Advanced Materials Conference, Palm Coast, FL, February 18, 1992, "Polymerization of Conducting Polymers at Free Surfaces"
11. ONR Program Review, Isle of Palms, SC, May 1, 1992, "Oxidative Coupling Polymerization at a Free Surface"
12. ACS National Meeting, Washington, DC, August 1992, "Real Time Investigations of Oxidative Coupling Polymerization Reactions Confined to Free Surfaces"
13. ACS National Meeting, Washington, DC, August 1992, "Temperature Effect on the Langmuir-Blodgett Polymerization of 2-Pentadecylaniline"
14. International Conference on Science and Technology of Synthetic Metals, Goteburg, Sweden, Aug. 12-18, 1992, "Thin Films of Functionalized Polyanilines Prepared by Restricting the Polymerization to Gas/Liquid and Liquid/Liquid Interfaces"
15. University Pierre and Marie Curie, Paris, France, June 8, 1992
16. Institute Charles Sadron, Strassbourg, France, June 19, 1992
17. Riken Research Institute, Tokyo, Japan, July 10, 1992
18. Kanagawa Academy of Science and Technology, Tokyo, Japan, July 11, 1992
19. ABO Akedemi University, Turku, Finland, Aug. 12, 1992
20. UCLA, Los Angeles, CA, Oct. 12, 1992
21. UCSB, Santa Barbara, CA, Oct. 16, 1992
22. Florida Advanced Materials Conference, Palm Coast, FL, March 1993, "Reactions to Form Conducting Polymers at Planar Liquid/Liquid Interface"
23. 6th International Conference on LB Films, Trois Riviers, Canada, July 1993, "Chemical and Electrochemical Mediated Polymerization of 2-Pentadecyl Aniline Confined to a Planar Liquid/Liquid Interface"
24. 6th International Conference on LB Films, Trois Riviers, Canada, July 1993, "Monolayer Polymerization of 2-Pentadecyl Aniline at Air/Aqueous Surfaces: Kinetics, Thermodynamics, Mechanism"
25. STM '93, International Conference on Scanning Tunneling Microscopy, Beijing, China, Aug. 9-13, 1993, "Langmuir-Blodgett (LB) Monolayers of a Conducting Polymer and Its Corresponding Monomer Studied by STM"
26. Naval Research Laboratories, Washington, DC, Feb. 10, 1993, "Langmuir Polymerization of Functionalized Anilines"

27. Northwestern University, Evanston, IL, Feb. 11, 1993, "Langmuir Polymerization of Functionalized Anilines"
28. University of Wisconsin, Madison, WI, Feb. 12, 1993, "Langmuir Polymerization of Functionalized Anilines"
29. University of Minnesota, Minneapolis, MN, Feb. 16, 1993, "Langmuir Polymerization of Functionalized Anilines"
30. Massachusetts Institute of Technology, Boston, MA, Feb. 24, 1993, "Langmuir Polymerization of Functionalized Anilines"
31. Kyoto University, Kyoto, Japan, July 16, 1993, "Langmuir Polymerization and STM Investigations of Conducting Polymers"
32. ACS National Meeting, San Diego, CA, Mar. 13-18, 1994, "Kinetics of Monolayer Polymerizations"
33. ACS National Meeting, San Diego, CA, Mar. 13-18, 1994, "Conducting Polymers Restricted to Gas/Liquid and Liquid/Liquid Interfaces"
35. Eastman Chemical Company, February 1994, "Synthesis of Conducting Polymer Monolayers"
36. Florida State University, Department of Chemistry, Tallahassee, FL, February 2, 1995, "Synthesis of Polyaniline in Monolayers" Thermodynamics, Kinetics and Mechanics"
37. Case Western University, Cleveland, OH, April 14, 1995, "Synthesis of Conducting Polymers in Restricted Dimensions"
38. International Symposium on Condensation Polymers (ISCP), Yonezawa, Japan, October 1995, "Oxidative Coupling in Restricted Dimensions: Synthesis of Conducting Polymers at Interfaces"
39. ACS National Meeting, Anaheim, CA, April 1995, "Polymerization and Phase Behavior of Poly(2-Pentadecylaniline) and Liquid Crystal Mixtures at the Air-Water Interface"
40. ACS National Meeting, Anaheim, CA, April 1995, "Alkyl Side Chain Positional Effect on the Polymerization of Alkyylaniline by Langmuir-Blodgett Techniques"
41. University of Florida Industrial Affiliates Meeting (Poster Award Winner), 1995, "Polymerization and Phase Behavior of 2-Pentadecylaniline and Liquid Crystal Mixtures at the Air/Water Interface"
42. NATO Advanced Study Institute, International Symposium on Micelles, Microemulsions, and Monolayers", *Solvents and Self Organization of Polymers*, Antalya, Turkey, 1995, "Langmuir and Langmuir-Blodgett-Kuhn Films of Poly(2-pentadecylaniline) and (R)-4'-(1-ethoxycarbonyl-1-ethoxy)phenyl-4-[4-(9-decenoxy)phenyl]benzoate (10PPB2)"
43. Quarter Century of Progress and New Horizons, University of Florida, 1995, "Langmuir and Langmuir-Blodgett-Kuhn Films of Poly(2-pentadecylaniline) and (R)-4'-(1-ethoxycarbonyl-1-ethoxy)phenyl-4-[4-(9-decenoxy)phenyl]benzoate (10PPB2)"
44. International Symposium on Micelles, Microemulsions and Monolayers: Quarter Century Progress and New Horizons, Gainesville, Florida, August 1995, "Langmuir Monolayer Films of *Ortho, Meta and Para* Pentadecylaniline"
45. International Symposium on Micelles, Microemulsions and Monolayers: Quarter Century Progress and New Horizons, Gainesville, Florida, August 1995, "Polymerization of *Meta* and *Ortho* Alkyylaniline by Langmuir-Blodgett Techniques: A Kinetic Study"
46. University of Bordeaux, Bordeaux, France, March 12, 1996, "Monolayer Synthesis of Conducting Polymers"
47. American Chemical Society National Meeting, Orlando, Florida, 1996, "Phase and Domain Behavior of Conduction Polymer and Liquid Crystal Mixtures at the Air/Water Interface"
48. American Chemical Society 212th National Meeting, Orlando, Florida, 1996, "The Effect of Structure on the Reactivity of Substituted Aniline Surfactants in a Monolayer Polymerization"

3 Significant Publications and Presentations:

Publication #13 is a full paper in the Journal of the American Chemical Society which is significant as it represents one of the more complete reports of thermodynamic and kinetic investigation of monolayer polymerization in the literature. The isotherm behavior of the 3 alkyl substituted monomers is compared and the polymerization results are discussed.

Publication #22 is a full paper in the ACS Journal, Langmuir, which presents some of the best sub-molecular resolution STM images of conducting polymers available to that date. These images showed that the conformation of surface polymerized conducting polymer chains is significantly different from that generally assumed to be obtained by other methods.

Publication #13 is a note in the ACS Journal, Macromolecules, which is significant in that it is one of very few studies of chemical polymerization reactions of monolayers at planar liquid/liquid interfaces. It was shown that the *ortho* alkyl anilines could be oxidatively polymerized at an Aqueous/hydrocarbon interface.

Presentations #7 and #10 are significant in that they were full invited talks at major international meetings. Presentation #25 was among the first involving STM on polymers at a major international meeting.

- View graph A-1 (five part view graph)

As shown, aniline and its derivatives generally polymerize under acidic conditions. To better understand the effect that acid has on the polymerization mechanism of substituted aniline surfactants, a series of experiments have been proposed that will allow for easy control of the acidity in the area the aniline moieties at the air-aqueous interface. Early progress in this research includes, the synthesis of monomer 17-(2-aminophenyl) heptadecanoic acid. Mean molecular area vs. surface pressure isotherm of this monomer have shown that the monomer exhibits multi-phase behavior (see diagram). It is believed that the aniline and acid ends are both adsorbed at the interface at low surface pressures (0-10 mN/m) then undergoes a phase transition as the area is decreased. As the monomer is confined to less area, the aniline end is pushed out and finally only the acid ends are adsorbed to the aqueous phase and the aniline ends are pushed up and away from the surface as shown in the diagram. Early results show that the monomer polymerizes at low surface pressures (~ 5 mN/m) but doesn't at higher surface pressures (~25 mN/m). The conditions require a strong chemical oxidant like ammonium persulfate, but in both cases, no additional acid is added. This has proven to be a way of polymerizing substituted aniline without adding additional acid to the subphase. This system may also allow the polymerization to be switched on and off by simply changing surface pressure. Once the polymerization kinetics have been studied, we plan to polymerize to monomer at the interface and then transfer it to metal oxide surfaces, using the carboxylic acid group to bind it to the surface.

- View graph A-2

The graph shows the change in the mean molecular area vs. time for 17-(2-aminophenyl) heptadecanoic acid under oxidative conditions at low and high surface pressures. As shown, there is a large change in the mean molecular area per molecule at low surface pressures. From earlier studies of oxidative polymerizations of monomers at the aqueous-air interface, the change area may indicate that polymerization of the monolayer is occurring, and in fact polymer has been collected from the surface as indicated by size-exclusion chromatography. At higher surface pressures, no great change in mean molecular area is seen, indicating that no reaction has occurred. We are currently studying this question in more depth.

- View graph A-3

This view graph shows the polymer with acid functional groups adsorbed to a solid substrate. We hope to polymerize the substituted aniline monomers on the Langmuir trough and then transfer this preformed polymer over to a metal oxide surface using the carboxylic acid group to bind it to the surface of the substrate.

ACCOMPLISHMENT: SELF-PROTONATING ANILINE MONOMER

OBJECTIVE: Studying the effect that subphase acidity has on aniline polymerization kinetics

CHALLENGE: Polymerize an aniline monomer in a Langmuir film while controlling the surface acidity

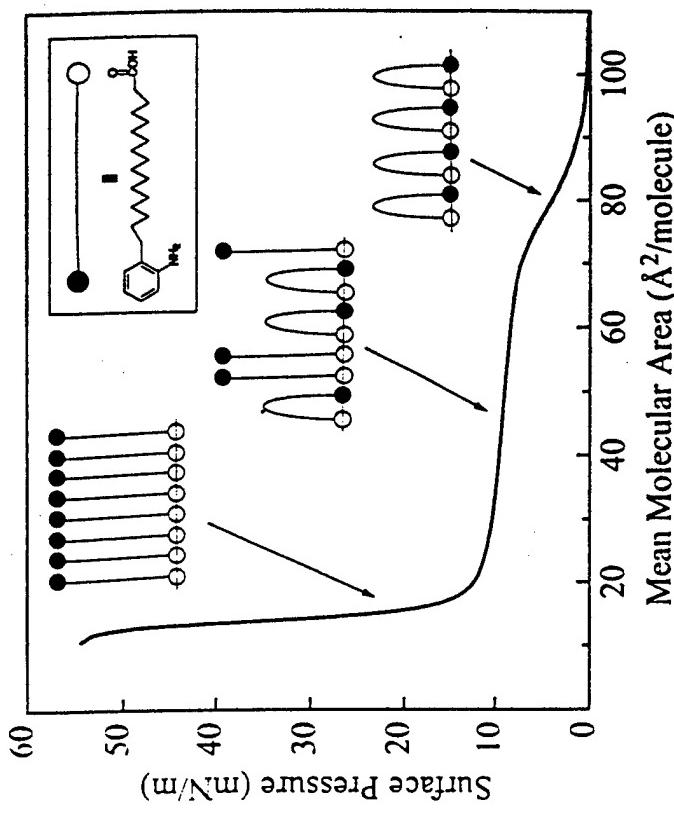
APPROACH: Covalent attachment of acid moieties to the monomer that serve to control the surface acidity

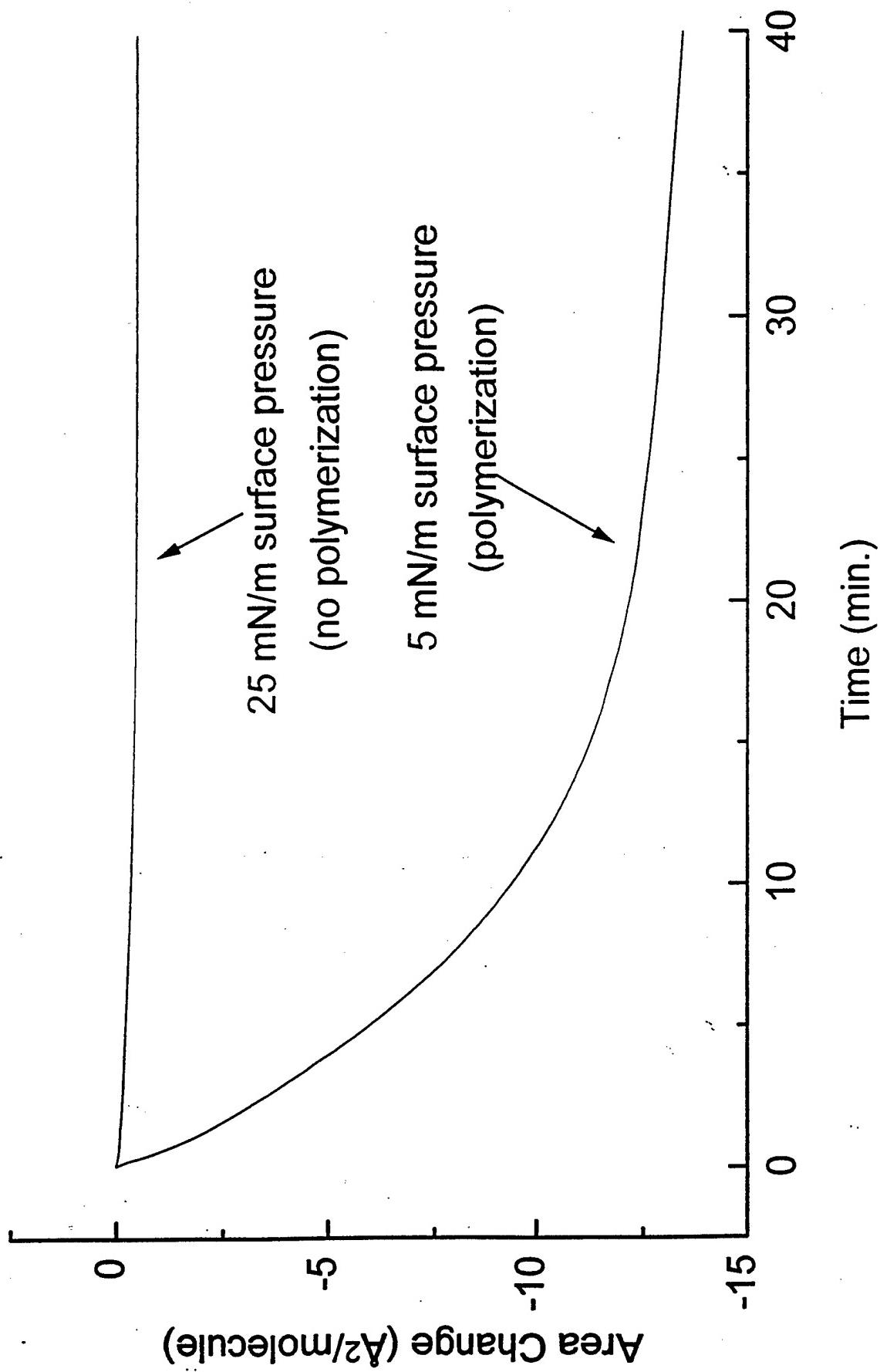
PROGRESS:

- Monomer 17-(2-aminophenyl) heptadecanoic acid synthesized and characterized
- Langmuir films display multi-phase behavior (see diagram)
- Films polymerized on neutral pH subphase

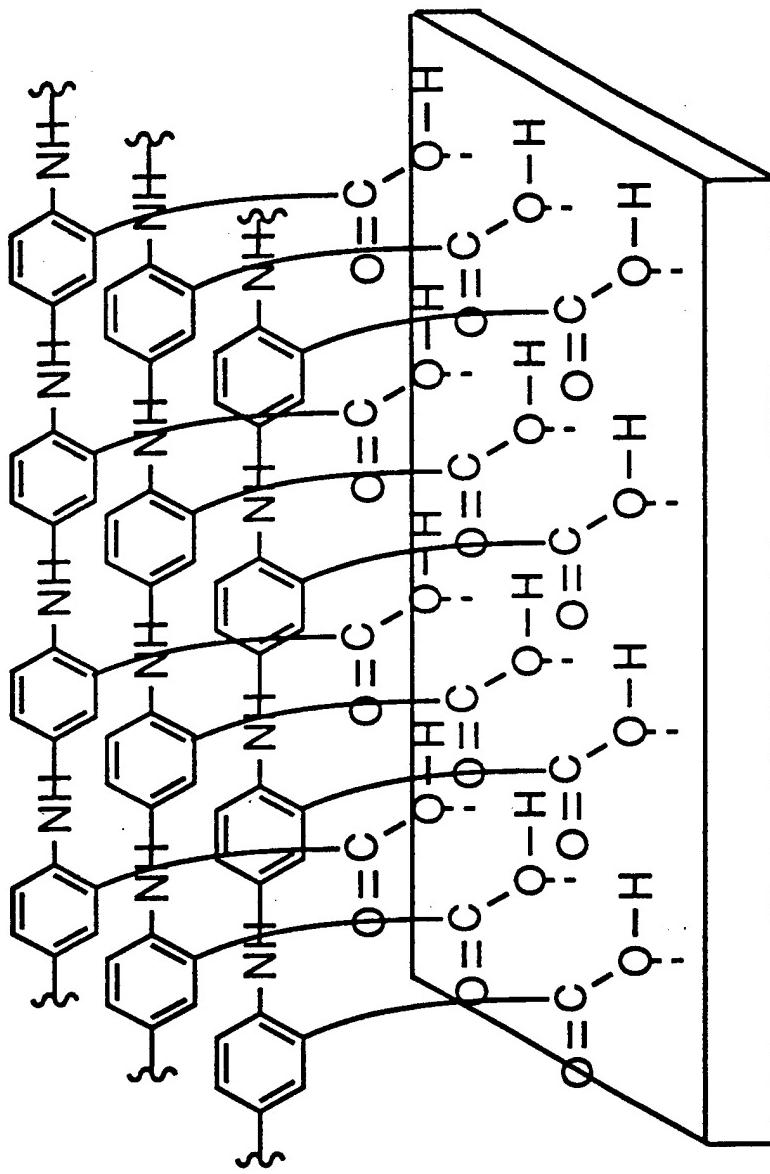
IMPACT:

A new concept of switching a reaction on and off by changing the surface pressure; a way of polymerizing aniline without adding additional acid; a polymer that has potential strong interactions with metal oxide substrates





Change in the mean molecular area of 17-(2-aminophenyl) heptadecanoic acid at 25 °C and under oxidative conditions (0.03 M ammonium persulfate) at high and low surface pressures.



Cartoon above shows poly[17-(aminophenyl) heptadecanoic acid] adsorbed on to a solid substrate.

B-1

View graph shows our main objective is to obtain an ordered array of conducting polymer quantum dots. Thermodynamic studies have been performed to determine if phase separation is favorable. The monomer has been successfully polymerized in the presence of the liquid crystal. The monolayers were then successfully transferred onto mica and studied using Tapping Mode™ Atomic Force Microscopy. The figure is a surface plot of a 40% liquid crystal (10PPB2) and 60% poly(2-pentadecylaniline) monolayer on a mica substrate. The circular liquid crystalline domains can be seen rising above the polymer. Future work will involve the study of these particular systems as well as striving to obtain the ordered array of conducting polymer quantum dots.

B-2

TMAFM imaging has been performed on a range of molar- compositions. The 4 figures show the effects of varying the molar concentration of the liquid crystal. Domains grow in number, but not in size as the molar concentration is increased. At very high liquid crystal concentrations the domains coalesce and become irregularly shaped. The polymerization conditions have been altered to obtain, although irregular, sub micron sized domains. This demonstrates we have the ability to change domain size and shape by manipulation of polymerization and deposition conditions. Surface Plasmon microscopy investigations have been scheduled to determine the liquid crystalline properties of these two-dimensional domains .

B-3

The figure show our representation of an assembly of these polymer/liquid crystal systems. These types of assemblies will be constructed in order to study the anisotropic effects on the liquid crystalline properties. Adsorbed monolayers of these systems shows long term stability on the substrate surface, in contrast to pure liquid crystals which tend lose their stability due to de-wetting of the substrate surface. These types of systems could be developed into applications involving polymer-dispersed liquid crystals and flat panel displays.

ACCOMPLISHMENT:

Phase Separated Conducting Polymer and Liquid Crystal Monolayer Mixtures

OBJECTIVE: Preparation of an ordered array of "quantum-dot" like conducting polymer domains within an insulating matrix adsorbed on a solid substrate

CHALLENGE: Technique has only been applied to simple phospholipid/cholesterol mixtures

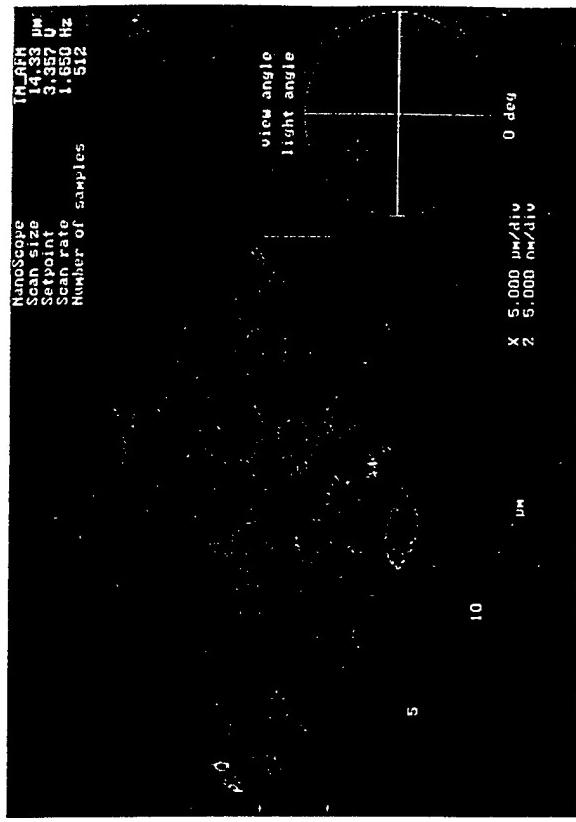
APPROACH: Use liquid crystalline properties to induce order into conducting polymer domains

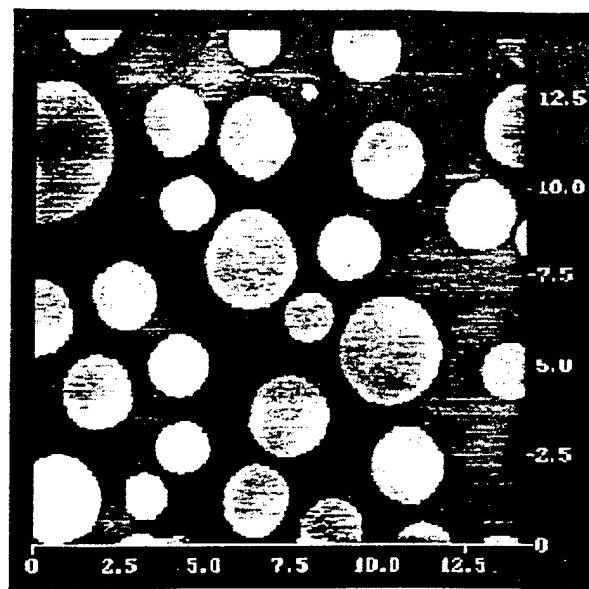
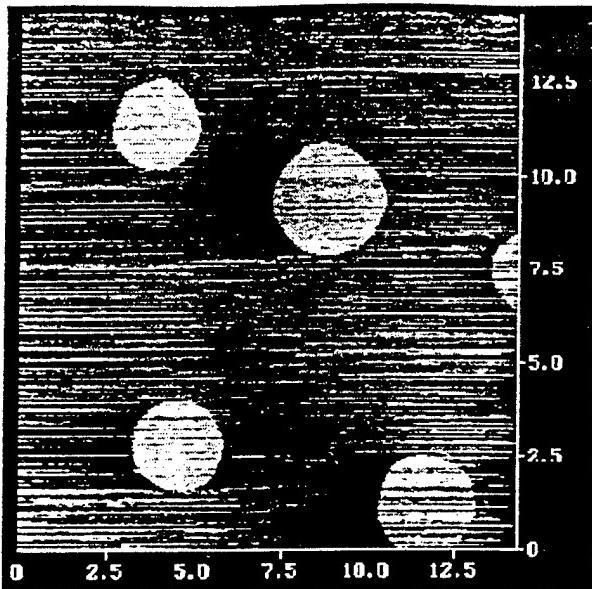
PROGRESS:

- Completed in-depth monolayer characterization and thermodynamic study of mixtures
- Successfully polymerized monomer in presence of liquid crystal
- Successfully transferred monolayer onto solid substrate and imaged phase separated LC domains using Atomic Force Microscopy

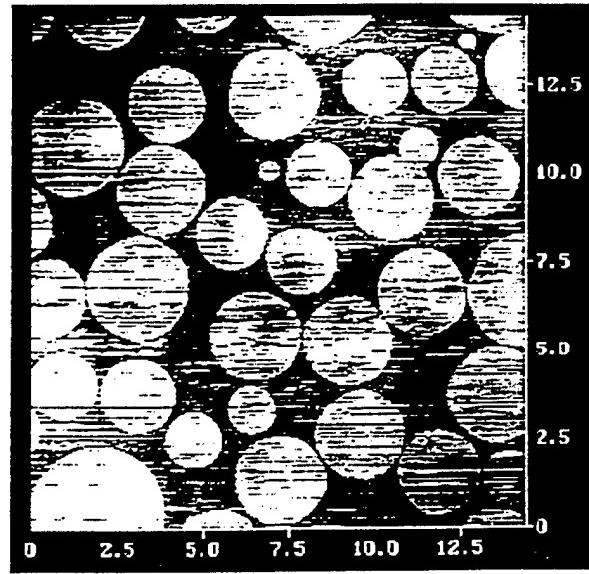
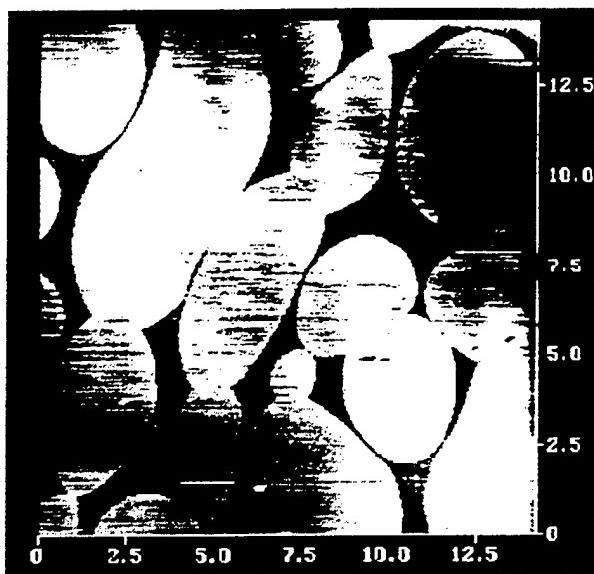
IMPACT:

Potential for current results lie in polymer-dispersed liquid crystals for flat panel displays.
Potential for future work lie in conducting or semiconducting nano-particle dispersions and new organic microelectronic devices.



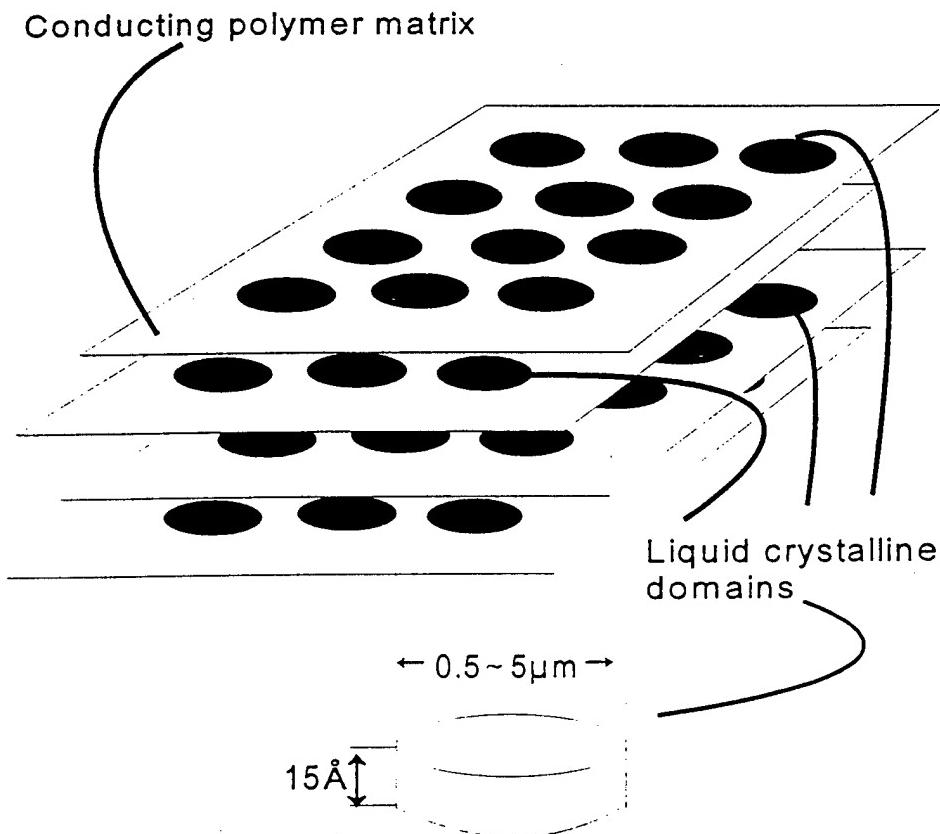


Z Range = 5 nm



- Composition dependence of liquid crystal on domain size and shape: Starting clockwise from the top left, 20%, 40%, 60%, and 80% (mole %).
- Domains grow in number, but not in size. At high liquid crystal concentration domains coalesce to form large irregular shaped domains

Conducting Polymer Templates



- Future work would involve preparation of a “swiss cheese” like assembly of conducting polymer multilayers using the phase separated monomer/liquid crystal systems.
- Extremely anisotropic liquid crystalline domains (micron diameters, nanometer thickness) surrounded by electroactive polymer could display unique properties.
- Confirmed environmental stability is greater than 3 months